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Inventor: ROBERT STIRLING WELLS

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COMPLETE SPECIFICATION

NO DRAWINGS

Improvements in Luminescent Materials

We, ASSOCIATED ELECTRICAL INDUSTRIES LIMITED, of 33 Grosvenor Place, London, S.W. 1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement;—

This invention relates to luminescent materials or phosphors. Such materials are capable, when subjected to incident radiation of one wavelength, of emitting radiation of another wavelength or wavelengths, or of emitting radiation when subjected to a stream of charged particles, such as cathode rays.

Cadmium silicate activated by manganese is one of the earliest known phosphors—emitting radiation of an orange colour when subject to irradiation by, for instance, short-wave ultra-violet radiation (such as emitted by the low-pressure mercury vapour arc) or by cathode rays.

Strontium silicate, so far as is known, has never been made to give useful luminescence unless intimately combined with substantial amounts (more than could be considered as activating amounts) of other metal silicates, e.g. calcium silicate or barium and/or lithium silicates.

Cadmium silicate activated with manganese is not generally used on television cathode ray tube screens or as a coating on the inside of low pressure mercury vapour lamps as the source or partial source of light from such tubes or lamps, because phosphors which give radiation of a similar colour but more efficiently, and which are cheaper to make and are more stable, are available.

There is still, however, a shortage of phosphors capable of giving a truly red luminescence, particularly when excited by short-wave ultra-violet radiation. Such materials as are known are either costly, poisonous, inefficient or unstable.

We have found that if strontium silicate is combined in solid solution with cadmium silicate, when activated with manganese, efficient red luminescent phosphors can be prepared. The luminescence of these phosphors is excited by both short-wave ultra-violet radiation and cathode rays.

The invention accordingly consists in a solid solution of cadmium silicate and strontium silicate activated with manganese, the molecular ratio of cadmium oxide to strontium oxide in the silicate being not more than 99:1 and not less than 0.5 to 1, and the atomic amount of manganese present lying between 0.125 and 0.0125 for each molecule of (cadmium oxide+strontium oxide).

For phosphors intended for excitation with ultra-violet radiation, the best results are obtained when the molecular ratio of cadium oxide (CdO) to strontium oxide (SrO) lies between 39 and 2 to 1; for those intended for excitation with cathode rays the proportion of SrO should be lower than 1:1, since at this CdO content the luminescence becomes violet and appreciably less efficient.

With both types of excitation, as the SrO content of the phosphor is increased, the luminescence becomes more red. The redness with short-wave ultra-violet excitation increases as the SrO content of the phosphor increases up to about 25% SrO per ($CdO+SrO$): thereafter the phosphor becomes only slightly more red until 50% SrO, 50% CdO is reached, after which there is a steady decline in brilliance to the non-fluorescent strontium silicate activated with Mn. With cathode ray excitation the change in colour from that of the simple cadmium silicate activated with Mn, with increase in the proportion of SrO, is less, and is accom-

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panied by a decrease in brilliance. At about 50% SrO. 50% CdO the luminescent colour starts to become bluish (presumably due to the prevalence of the inefficient bluish-luminescence of the strontium silicate activated with Mn) and the brilliance with further SrO addition declines rapidly.

The molecular proportion of SiO_2 to (CdO+SrO) is preferably about 1.0 to 1.2 mols of SiO_2 for each molecule of (CdO+SrO) departure may be made from this ratio, and depending on the reactivity of the SiO_2 used, may be beneficial. If the SiO_2 content is too far reduced the manganese may be difficult to incorporate in the phosphor, giving it a brown appearance in daylight. If too much SiO_2 is used, the excess over that required to combine with the CdO, SrO and manganese compound, dilutes the phosphor and makes it less efficient. The useful range is from 0.9 to 1.4 mol. SiO_2 for each mol of (CdO+SrO).

With short-wave ultra-violet excitation the manganese content of the phosphor also influences the colour and brilliance; low manganese contents giving a relatively orange colour with low brilliance, and high manganese contents favouring the red with high brilliance. We prefer to use $MnCl_2.4H_2O$ as the source of Mn, but do not wish to exclude the use of other suitable Mn compounds such as $MnCO_3$.

With short-wave ultra-violet excitation the Mn content should lie between 0.125 atoms and 0.0125 atoms of Mn for each molecule of (CdO+SrO), with a preferred amount of about 0.05 to 0.06 atoms Mn (on the same basis).

With cathode ray excitation the brilliance of the phosphors is less affected than the colours by the Mn content, a low Mn content giving a yellowish colour and a high content a reddish one with a given CdO:SrO ratio. The Mn content should lie between 0.005 atoms and 0.08, on the previous basis.

The phosphors can be prepared by firing in air, a dry mixture of $CdCO_3$, $SrCO_3$ and SiO_2, to which $MnCl_2.4H_2O$, conveniently as a 50% w/v solution in water, has been added, at a temperature of about 900°C. for periods of 1 to 4 hours at a time. The firing temperature should be chosen so that the phosphor is not unduly sintered, and too low a temperature gives a slow reaction. This temperature of about 900°C is suitable for CdO:SrO ratios near the middle of the preferred range, but higher temperatures may be used for mixtures with extreme amounts of CdO or SrO.

The presence of halogen, particularly Cl or F seems to be essential to the production of efficient phosphors, and to the full development of the redness to be obtained by the introduction of the SrO.

The colour of luminescence is also influenced by the Mn content, the higher the Mn the more the colour moves to the red, within the limits given.

By varying the content of SrO, Mn, and halogen in the phosphors, the peak emission of energy by the phosphors can be controlled within the range of about 6000°A to about 6500°A when excitation is by the low pressure mercury vapour arc.

Care should be taken to keep the pre-firing mixes free from organic matter since this causes reduction, and loss of cadmium during the firing process.

In addition the raw materials should be pure, fine and reactive and of a general quality suitable for the preparation of luminescent materials. Allowance should be made for the moisture etc. content of the SiO_2.

The following are examples of the preparation of luminescent materials according to the invention.

EXAMPLE 1:

Mix together intimately in the dry way by grinding, ball-milling or other suitable means:—

27.5 gms. $CdCO_3$ (0.16 gm. Mol)
5.9 " $SrCO_3$ (0.04 gm. Mol)
16.0 " SiO_2 (containing 91.18% anhydrous SiO_2). (0.24 gm. Mol)

Add 4.5 mls. of aqueous $MnCl_2.4H_2O$ solution containing 50% $MnCl_2.4H_2O$ w/v (0.0114 gm. Mol).

Mix intimately.

Fire at 900°C for 1½ hours in a closed fused quartz crucible, in an atmosphere of air. Grind to a fine powder and fire again at 900°C for 2 hours, as before. Repeat the firing and grinding until maximum brilliance is attained. Three or four firings in all should be sufficient.

After powdering and seiving the phosphor should be very nearly white by daylight, should show a strong red luminescence excited by short-wave ultra-violet radiation, and a moderately efficient red luminescence excited by cathode rays.

If a phosphor is required for cathode ray use, the SiO_2 amount in the above example should be reduced to 14.5 gms. with the other quantities and treatment kept the same.

Alternative methods of preparation are in which some or all of the $SrCO_3$ is replaced by the equivalent quantity of either $SrCl_2$ or SrF_2, and the $MnCl_2.4H_2O$ is preferably replaced by the equivalent quantity of $MnCO_3$ or other suitable Mn compound. The total amount of Cl or F should not be less than the chemical equivalent of the Mn.

The following are examples of these alternative methods of preparation:—

EXAMPLE 2:

Mix intimately as before:—

33.6 gms. $CdCO_3$	(0.195 gm. Mol)
1.33 gms. $SrCl_2.6H_2O$	(0.005 gm. Mol)
12.61 gms. Anhydrous SiO_2	(0.210 gm. Mol)
2.25 gms. $MnCl_2.4H_2O$	(0.0114gm. Mol).

Fire in a silica crucible in an electric muffle furnace to which normal access of air is allowed, at 950°C for 1½ hours, followed by 1025°C for 2 hours, and 1050°C for 2 hours, with grinding between firings.

EXAMPLE 3:

Mix intimately as before:—

29.3 gms. $CdCO_3$	(0.170 gm. Mol)
3.77 gms. SrF_2	(0.030 gm. Mol)
12.61 gms. SiO_2 Anhydrous	(0.210 gm. Mol)
1.45 gms. $MnCO_3$ containing 95.1% anhydrous $MnCO_3$	(0.0120 gm. Mol).

Treat as Example 2, but fire at 950°C for 1½ hours followed by further firings at 950°C of 3 and 2½ hours respectively.

WHAT WE CLAIM IS:—

1. A red luminescing material consisting of a solid solution of cadmium silicate and strontium silicate activated with manganese, the molecular ratio of cadmium oxide to strontium oxide in the silicate being not more than 99:1 and not less than 0.5 to 1, and the atomic amount of manganese present lying between 0.125 and 0.0125 for each molecule of (cadmium oxide+strontium oxide).

2. A red luminescing material consisting of a solid solution of cadmium silicate and strontium silicate activated with manganese, the molecular ratio of cadmium oxide to strontium oxide in the silicate being not more than 99:1 and not less than 0.5 to 1, the molecular amount of silica present lying between 0.9 and 1.4 for each molecule of (cadmium oxide+strontium oxide), and the atomic amount of manganese present lying between 0.125 and 0.0125 for each molecule of (cadmium oxide+strontium oxide).

3. A red luminescing material for excitation by ultra-violet radiation consisting of a solid solution of cadmium silicate and strontium silicate activated with manganese, the molecular ratio of cadmium oxide to strontium oxide in the silicate being not more than 39:1 and not less than 2:1, the molecular amount of silica present lying between 0.9 and 1.4 for each molecule of (cadmium oxide+strontium oxide), and the atomic amount of manganese present lying between 0.125 and 0.0125 for each molecule of (cadmium oxide+strontium oxide).

4. A red luminescing material for excitation, by cathode rays consisting of a solid solution of cadmium silicate and strontium silicate activated with manganese, the molecular ratio of cadmium oxide to strontium oxide in the silicate lying between 99 and 0.5 to 1, the molecular amount of silica present lying between 0.9 and 1.4 and the atomic amount of manganese present lying between 0.08 and 0.005 for each molecule of (cadmium oxide+strontium oxide).

5. A red luminescing material prepared in accordance with any of the hereinbefore given Examples.

J. W. RIDDING,
Chartered Patent Agent,
Crown House, Aldwych,
London, W.C.2.
Agent for the Applicants.

PROVISIONAL SPECIFICATION

Improvements in Luminescent Materials

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This invention relates to luminescent materials, or phosphors. Such materials are capable, when subjected to incident radiation of one wavelength, of emitting radiation of another wavelength or wavelengths, or of emitting radiation when subjected to a stream of charged particles, such as cathode rays.

Cadmium silicate activated by manganese is one of the earliest known phosphors—emitting radiation of an orange colour when subject to irradiation by, for instance, short-wave ultra-violet radiation (such as emitted by the low-pressure mercury vapour arc) or by cathode rays.

Strontium silicate, so far as is known, has never been made to give useful luminescence unless intimately combined with substantial amounts (more than could be considered as activating amounts) of other metal silicates, e.g. calcium silicate or barium and/or lithium silicates).

Cadmium silicate activated with manganese is not generally used on television cathode ray tube screens or as a coating on the inside of low pressure mercury vapour lamps as the source or partial source of light from such tubes or lamps, because phosphors which give radiation of a similar colour but more efficiently, and which are cheaper to make and are more stable, are available.

There is still, however, a shortage of phosphors capable of giving a truly red luminescence, particularly when excited by short-wave ultra-violet radiation. Such materials as are known are either costly, poisonous, inefficient or unstable.

We have found that if strontium silicate is combined in solid solution with cadmium

silicate, when activated with manganese, efficient red luminescent phosphors can be prepared. The luminescence of these phosphors is excited by both short-wave ultra-violet radiation and cathode rays. The invention accordingly consists in a luminescent material comprising a cadmium-strontium silicate activated with manganese, the molecular ratio of cadmium oxide to strontium oxide in the silicate lying between 9 and ½ to 1, the molecular amount of silica present lying between 1.8 and 2.8, and the atomic amount of manganese present being between 0.125 and 0.0125, for each molecule of strontium and cadmium oxides.

For phosphors intended for excitation with ultra-violet radiation, the best results are obtained when the molecular ratio of cadmium oxide (CdO) to strontium oxide (SrO) lies between 4 and 1 to 1, for those intended for excitation with cathode rays the proportion of SrO should be lower than 1:1, since at this SrO content the luminescence becomes violet and apppreciably less efficient.

With both types of excitation, as the SrO content of the phosphor is increased, the luminescence becomes more red. The increase in redness with short-wave ultra-violet excitation is approximately proportional to the SrO content of the phosphor up to about 25% SrO per CdO+SrO; thereafter the phosphor becomes only slightly more red until 50% SrO 50% CdO is reached, after which there is a steady decline in brilliance to the non-fluorescent strontium silicate activated with Mn. With cathode ray excitation the change in colour from the simple cadmium silicate activated with Mn is less, and is accompanied by a decrease in brilliance. At about 50% SrO, 50% CdO the luminescent colour starts to become bluish (presumably due to the prevalence of the inefficient blue-luminescence of the strontium silicate activated with Mn) and the brilliance with further SrO addition declines rapidly.

The molceular proportion of SiO_2 to CdO +SrO is preferably about 2.4 mols of SiO_2 for each molecule of CdO and SrO. Departure may be made from this ratio, and depending on the reactivity of the SiO_2 used, may be beneficial. If the SiO_2 content is too far reduced the manganese may be difficult to incorporate in the phosphor, giving it a brown appearance in daylight. If too much SiO_2 is used, the excess over that required to combine with the CdO, SrO and manganese compound, dilutes the phosphor and makes it less efficient. The useful range is from 1.8 to 2.8 mol. SiO_2 for unit total mols of CdO plus SrO.

With short-wave ultra-violet excitation the manganese content of the phosphor also influences the colour and brilliance; low manganese contents giving a relatively orange colour with low brilliance, and high manganese contents favouring the red with high brilliance. We prefer to use $MnCl_2.4H_2O$ as the source of Mn, but do not wish to exclude the use of other suitable Mn compounds such as $MnCO_3$.

With short-wave ultra-violet excitation the Mn content should like between 0.125 atoms and 0.0125 atoms of Mn for each molecule of CdO and SrO, with a preferred amount of about 0.05 to 0.06 atoms Mn (on the same basis).

With cathode ray excitation the brilliance of the phosphors is less affected than the colours, a low Mn content giving a yellowish colour and a high content a reddish one with a given CdO:SrO ratio. The Mn content should lie between 0.005 atoms and .08 on the previous basis.

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J. W. RIDDING,
Chartered Patent Agent,
64-66, Coleman Street,
London, E.C.2.

Agent for the Applicant.

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